O-8.2 Sequence driven behavior of versatile Cu-peptide complexes acting as electrocatalysts in the Oxygen Evolving Reaction (OER)

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First row transition metal complexes as molecular catalytic systems for the oxygen evolving reaction (OER) are getting attention due to their availability and rich redox chemistry. The OER has central role in the artificial photosynthesis concept as the electron source for the production of renewable chemical energy carriers, H_2 in the first place. With the help of the versatile molecular catalysts the OER may take place at a higher rate, lower overpotential, or under less demanding conditions.

Copper complexes are of peculiar interest, including small Cu-peptides, in which the redox reactivity strongly depends on the amino acid sequence [1]. Importantly, in a molecular catalyst the ligand design defines the metal coordination sphere and secondary interactions, the functional groups in close proximity to the metal center and also, the number of metal sites in one molecule. Since basically the equatorial coordination of deprotonated amidic donor groups is responsible for the $Cu^{III/II}$ and further anodic redox events leading eventually to the active species, it is thus relevant to investigate how the available structural variations of peptides influence the basic descriptors of the OER.

We have explored how catalysis is affected by branching, or systematically modifying small peptides in other ways thus accessing a highly modular ligand family. Substantial changes were observed in the properties of the complexes upon introducing *C*-terminal or *N*-terminal substitutions, single, or multiple branching, different chelate ring size, etc., that were manifested sometimes in palpable differences between their catalytic capabilities [2,3]. We also demonstrated a heterogenization method for these functional Cu-peptides by selective, self-assembled layering together with polyelectrolytes onto an electrode surface [4].

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